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Development of a Microcomputer Controlled Multi-Probe Instrument for Automated Time-Dependent Measurement of Redox Potential and Oxygen Diffusion Rate

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16. ABSTRACT

The objective of the project was to evaluate control measurements available for parameters to serve as indicators of biodegradation for a land treatment facility. An earlier paper reported results of comparative studies between wax impregnated graphite electrodes (WIGE) and platinum wire electrodes (PWE) to determine ODR and redox potential (Eh). The study indicated that WIGEs are less susceptible to oxide poisoning, easily fabricated, relatively inexpensive, and more stable in soil than PWEs. A second paper reported the use of WIGEs and PWEs to measure Eh and ODR during biodegradation of glucose and phenol in a soil environment as compared to determining actual biodegradation of those compounds by analytical procedures. The results indicated that Eh and ODR can be suitable parameters for indication of biodegradation of organics by land treatment processes.

The spatial variability of soils necessitates making multiple measurements to obtain data "representative" of a given area. This paper reports the design and construction of a constant current-constant voltage potentiostat utilizing a microcomputer to control 64 separate electrode inputs from field (in situ) or laboratory soil samples. Either ODR or Eh can be measured and recorded in a solution or soil environment.

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ANALYTICAL INSTRUMENTATION, 15(1), 51-62 (1986)

DEVELOPMENT OF A MICROCOMPUTER CONTROLLED MULTI-PROBE INSTRUMENT FOR AUTOMATED TIME-DEPENDENT MEASUREMENT OF REDOX POTENTIAL AND OXYGEN DIFFUSION RATE

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ABSTRACT

A constant current-constant voltage potentiostat system using a Commodore 64 microcomputer was designed and built to aid in the characterization of the aeration status of either in field (in situ) or laboratory soil samples. The system can control 64 separate inputs in the measurement of either reduction-oxidation potential, E_H, or oxygen diffusion rate, ODR, in a solution phase or in a soil environment.

I. INTRODUCTION

A constant current-constant voltage potentiostat system using a Commodore 64 (C-64) microcomputer was designed and built to aid in the characterization of the aeration status of either in field (in situ) or laboratory soil samples.

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The system has the capacity to control 64 separate inputs in the measurement of either reduction-oxidation potential, E_H, or oxygen diffusion rate, ODR, in the soil phase. Inert, durable, and electrochemically reproducible electrodes also were developed for both laboratory and in field use with this instrument and are discussed elsewhere (1,2).

Soil aeration is the process by which gases consumed or produced in the soil are exchanged for gases in the atmosphere. Soil oxygen is obtained primarily by diffusion from the atmosphere through the gaseous and aqueous phases of the soil to the microbial population. The measurement of reduction-oxidation potential is important in that it provides a measure of the electron activity or the oxygen availability in the soil-solution phases. E_H is measured very simply by placing both an inert electrode and a reference electrode in a soil sample or solution and measuring the "at rest" potential difference between the electrodes. Aerated, well-drained soils have characteristic potentials in the range of +400 to +700 mV, while water logged and poorly drained soils with high carbon content have E_H potentials as low as -250 to -300 mV. In flooded soils or in soils with low oxygen levels, the sensitivity of the E_H potential becomes more generally useful than in well aerated and well drained soils where measurement of the oxygen diffusion rate gives the more sensitive indication of the soil aeration status.

The technique of measuring oxygen diffusion rates is predicated upon the concept that the limiting factor in the soil oxygen supply to the microbial population or root systems is the rate of diffusion of oxygen through the moisture films in the soil phase in contact with the respiring microorganisms. The oxygen diffusion rate then is related to the oxygen reduction rate at an inert electrode surface when a constant electrical potential is applied (3). Once the oxygen present at the inert electrode surface is reduced, further oxygen reduction depends on the rate of oxygen diffusion to the electrode surface which relates to the maximum available to any present respiring roots or to the microbial population.

II. CIRCUIT DESCRIPTION

The developed system uses a readily available Commodore 64 personal computer (C-64) with its associated disc drive, printer, and video monitor to control the instrument operation. A block diagram of the system is shown in Figure 1. Modifications were required so that the C-64 could be battery operated for both back up laboratory use in case of power failure or stand alone operation in a field monitoring situation. These modifications are shown in Figure 2. When the circuit in Figure 2 is used with a.c. line power, the phase lock loop will synchronize to the 60 Hz line frequency. When no line frequency is available (a.c. power failure or battery operation), the phase lock loop oscillates at the free running frequency of the voltage controlled oscillator (VCO), which was adjusted to 60 Hz. Deep cycle marine batteries were used to provide the d.c. voltage required by all onboard voltage regulators during battery operation.

A 40 column adding machine tape Citizen model IDP-560 printer, which is compatible with the C-64, was used. This printer contains a 12 volt drive motor and print head which required bypassing its a.c. supply during battery operation. A five volt regulator (National Semiconductor LM 340T-5) was added to operate the printer's communication and logic card during battery operation.

A 115 volt a.c. operated Sanyo VM 4209 video monitor was used with the computer. During battery operation of the system, the monitor was used only for computer initialization and instructional checkout. Monitor power was provided by a 12 volt d.c. to 115 volt a.c. power converter during battery operation.

The computer to potentiostat interface consists of three printed circuit boards: 1.) the main board which provides digital communication with the computer, analog to digital conversion, and digital to analog conversion (Figure 3), 2.) the multiplexer board (Figure 4), 3.) the relay board (Figure 5), and the associated power supply.

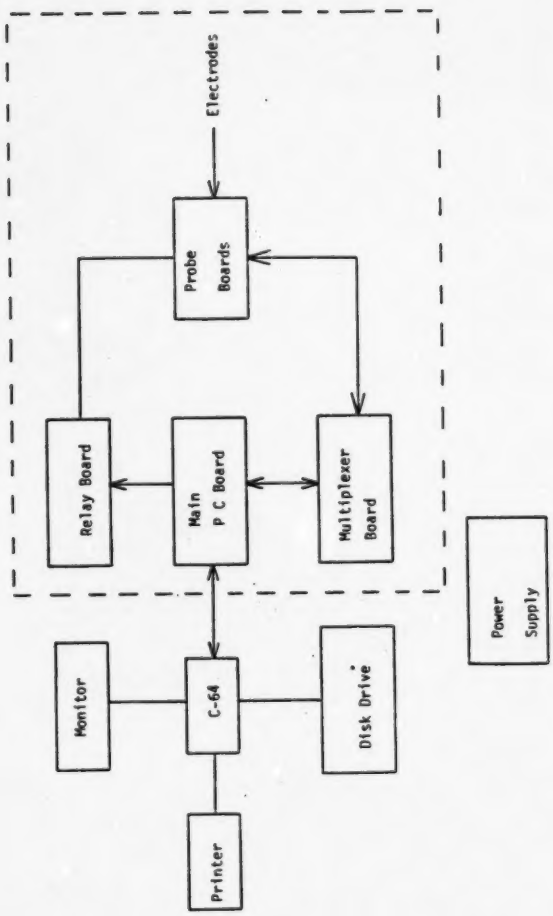

FIGURE 1.
Block Diagram

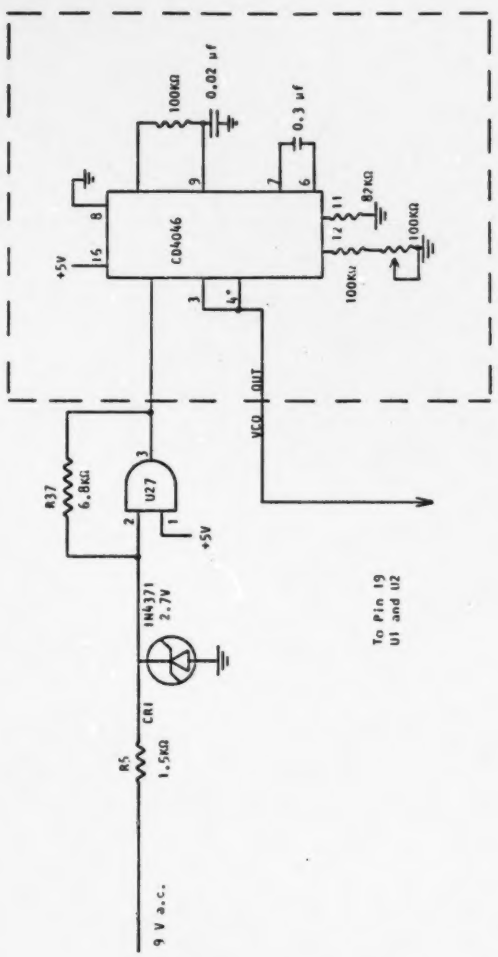

FIGURE 2.
Modifications to C-64 Time of Day Clock

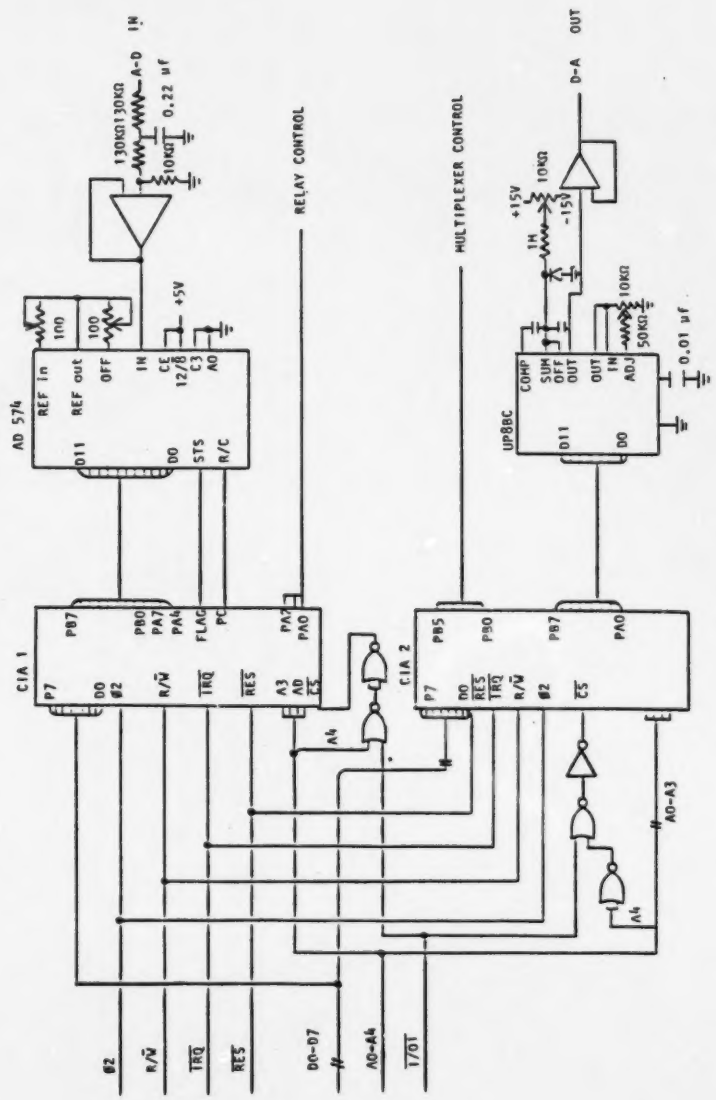

FIGURE 3.
Main PC Board

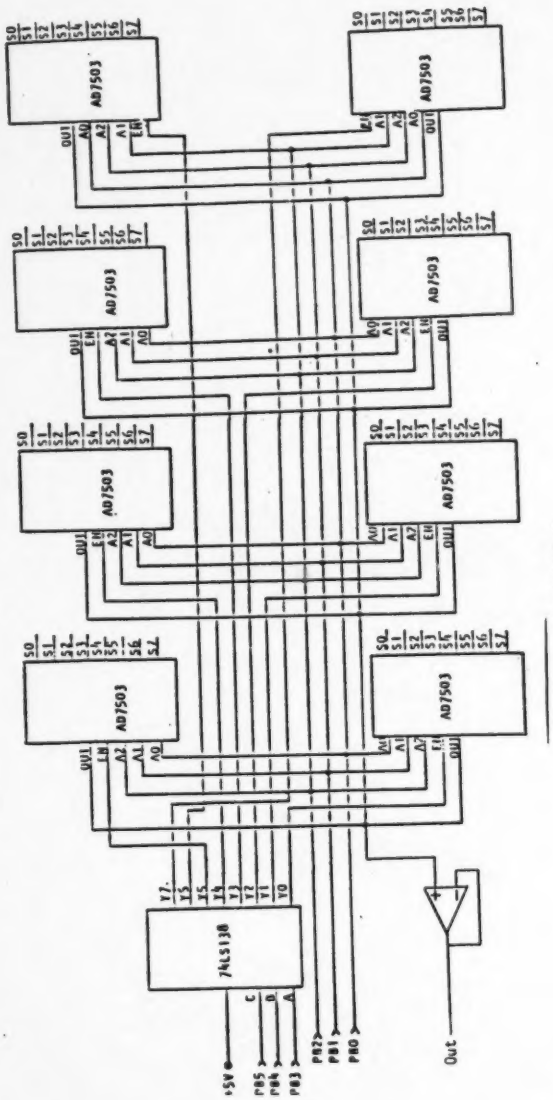

FIGURE 4.
Multiplexer Board

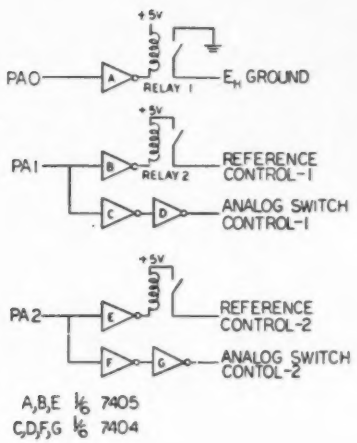

FIGURE 5.
Relay Board

The main circuit board consists of two MOS Technology 6526 Complex Interface Adapters (CIAs), an Analog Devices AD574 12-bit analog to digital (A-D) converter, a Datel-Intersil UP8BC 8-bit digital to analog (D-A) converter, CIA address decoding, and input and output buffers in both the A-D and D-A sections. The A-D converter is used to measure the E_H potential or ODR current and has a precision or resolution of $\pm$2.44 mV. The D-A converter is used to provide potentiostat voltage and has a precision or resolution of $\pm$39 mV.

The Complex Interface Adapters feature two 8-bit input/output ports, two 16-bit interval timers, a 24 hour time of day clock with alarm, and an 8-bit shift register. The first CIA (CIA-1) is located at addresses $DE00 to $DE0F. This address decoding is a logical OR of the computer's I/O1 line and address line A4. The second CIA (CIA-2) is addressed at $DE10 to $DE1F. The CIA2 is selected by a logical AND of the I/O1 line and address line A4.

The analog to digital converter is controlled by CIA-1's PC and FLAG lines. The PC output pin goes low for one cycle after each read or write of

Port B. This signals the A-D converter to start conversion by pulling the AD574's R/C input low. When conversion is completed the status (STS) line will go low, pulling CIA-1's FLAG line low. This sets the flag bit in the CIA-1 Interrupt Control Register and latches the data in Ports A and B.

CIA-2 is used to control the digital to analog converter and the analog multiplexers. Port A is used to output data to the UP8BC digital to analog converter, which is set up for continuous conversion. The lower three bits of Port B are used to select one of eight inputs on each multiplexer and bits three, four, and five are used to select one of eight multiplexers. This gives a total of 64 analog inputs to the A-D converter.

The lower three bits on Port A (PA 0,1,2) of CIA-1 are used to control the three relays and the analog switch controls on the relay board. PA0 is used to energize relay one which connects the anodes to circuit ground for E_H measurements. PA1 and PA2 are used to control the relays and the analog switches on the probe boards. During ODR measurements relays 2 and/or 3 are energized to connect the reference voltage to the potentiostat and close switches A and B on the probe boards. Each of the eight probe boards as shown in Figure 6 can connect to eight cathodes, a single anode, and a reference electrode. Additionally, there are eight voltage outputs from each probe board which return to the instrument, a relay control line, and a line from the D-A converter.

For ODR measurements, relay one on the relay board is turned off and either relay two, and/or three, are turned on and switches A and B are closed. A buffer amplifier is used to isolate the anode voltage from the D-A converter. The reference electrode is used as a sensor in the feedback path of the anode amplifier to maintain a constant voltage at the anode. The current at the cathode of the electrochemical cell is converted to a voltage by the National Semiconductor LF 347 operational amplifier which has a gain of 10 mV/μA.

For E_H measurements, switches A and B are opened which removes the current to voltage converters and the anode from the measurement circuit, allowing the

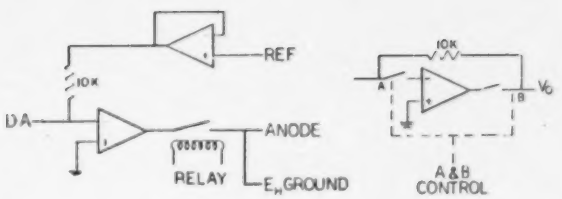

FIGURE 6.
Probe Board

measurement of the voltage at each of the cathodes with respect to the reference electrode which is connected to circuit ground by relay one.

A flowchart for the software, which was written in BASIC, is shown in Figure 7.

III. ELECTROCHEMICAL EVALUATION

All electrochemical measurements of the developed system were compared to the measurements performed with a PAR 174A polarographic analyzer (Princeton Applied Research Corporation, Princeton, N.J.). The PAR instrument employs a three-electrode polarographic circuit, in which a fixed potential can be applied between a microcathode and a reference electrode via a potentiostat. The electrochemical discharge current was measured between the cathode and the anode (the third electrode), thus bypassing the high-impedance reference electrode. The reference was a silver-silver chloride electrode (SSCE) adaptable to soil (Jensen Instruments, Tacoma, WA) and the anode was a 20 cm long brass rod.

Two types of potential studies were conducted: potential step and potential scan. In the potential step studies, the potential between the cathode and the reference electrode was maintained constant and the current was measured after stabilization due to the diffusion-controlled reduction or oxidation of chemical species present in the system. In the potential scan

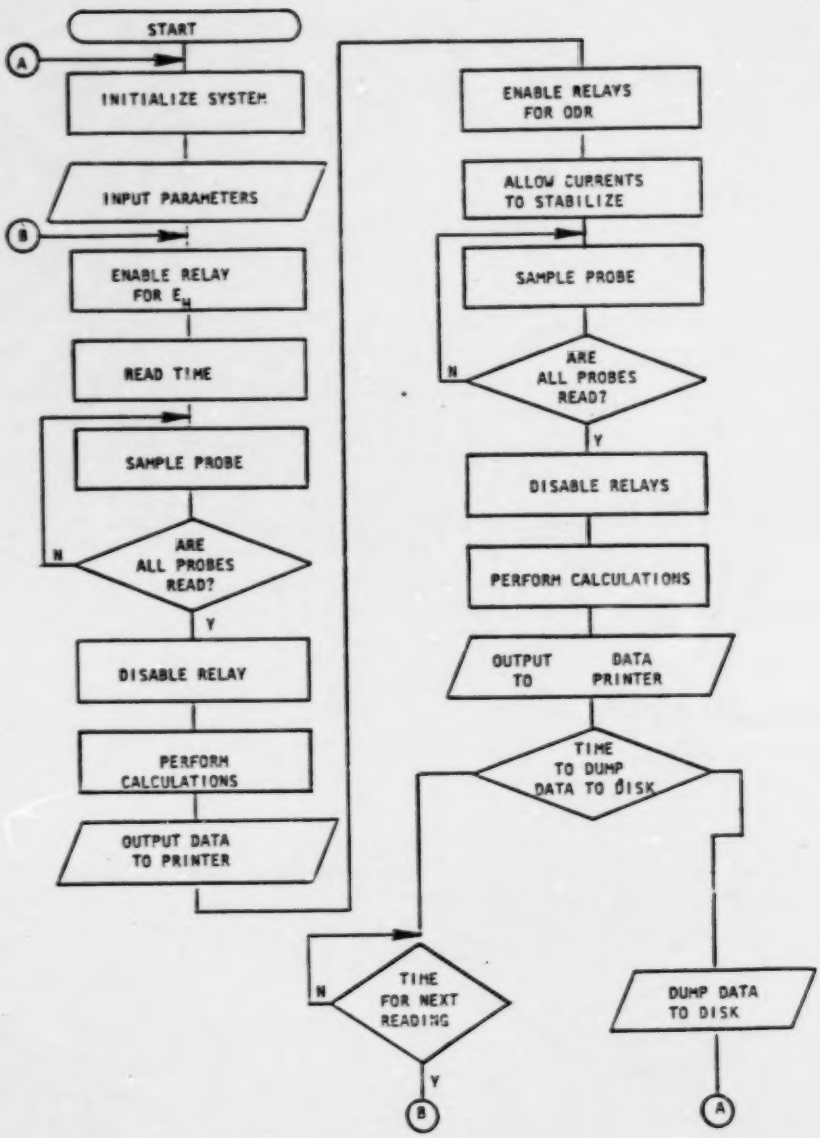

FIGURE 7.
Flow Chart

studies, the potential was continuously varied either linearly or in a periodic fashion while simultaneously monitoring the current. Reduction-oxidation potential, E_H, results were compared to the values obtained using a Corning Model 130 digital pH meter/voltmeter (Corning, N.Y.).

Electrodes were evaluated with the instrument in solutions containing a mixture of ferrocyanide and ferricyanide at various ratios and in either 1.0 M HCl or 1.0 M ammonium acetate media, and in soil suspension (under stirring conditions) containing a fixed amount of soil in a solution of ferrocyanide/ferricyanide mixture buffered with 1.0 M ammonium acetate. The ferrocyanide/ferricyanide reduction-oxidation couple is well poised for E_H measurements (4).

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